

Notice of Allowability

Application No.

10/532,511

Examiner

Porfirio Nazario-Gonzalez

Applicant(s)

DAMRAU ET AL.

Art Unit

1621

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

All claims being allowable, PROSECUTION ON THE MERITS IS (OR REMAINS) CLOSED in this application. If not included herewith (or previously mailed), a Notice of Allowance (PTOL-85) or other appropriate communication will be mailed in due course. **THIS NOTICE OF ALLOWABILITY IS NOT A GRANT OF PATENT RIGHTS.** This application is subject to withdrawal from issue at the initiative of the Office or upon petition by the applicant. See 37 CFR 1.313 and MPEP 1308.

1. ☐ This communication is responsive to ____.
2. ☒ The allowed claim(s) is/are 1-18.
3. ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
- a) ☐ All b) ☐ Some* c) ☐ None of the:
1. ☒ Certified copies of the priority documents have been received.
2. ☐ Certified copies of the priority documents have been received in Application No. ____.
3. ☐ Copies of the certified copies of the priority documents have been received in this national stage application from the International Bureau (PCT Rule 17.2(a)).

* Certified copies not received: ____.

Applicant has THREE MONTHS FROM THE "MAILING DATE" of this communication to file a reply complying with the requirements noted below. Failure to timely comply will result in ABANDONMENT of this application.

THIS THREE-MONTH PERIOD IS NOT EXTENDABLE.

4. ☐ A SUBSTITUTE OATH OR DECLARATION must be submitted. Note the attached EXAMINER'S AMENDMENT or NOTICE OF INFORMAL PATENT APPLICATION (PTO-152) which gives reason(s) why the oath or declaration is deficient.
5. ☐ CORRECTED DRAWINGS (as "replacement sheets") must be submitted.
- (a) ☐ including changes required by the Notice of Draftsperson's Patent Drawing Review (PTO-948) attached
- 1) ☐ hereto or 2) ☐ to Paper No./Mail Date ____.
- (b) ☐ including changes required by the attached Examiner's Amendment / Comment or in the Office action of Paper No./Mail Date ____.
- Identifying indicia such as the application number (see 37 CFR 1.84(c)) should be written on the drawings in the front (not the back) of each sheet. Replacement sheet(s) should be labeled as such in the header according to 37 CFR 1.121(d).
6. ☐ DEPOSIT OF and/or INFORMATION about the deposit of BIOLOGICAL MATERIAL must be submitted. Note the attached Examiner's comment regarding REQUIREMENT FOR THE DEPOSIT OF BIOLOGICAL MATERIAL.

Attachment(s)

1. ☒ Notice of References Cited (PTO-892)
2. ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
3. ☒ Information Disclosure Statements (PTO-1449 or PTO/SB/08), Paper No./Mail Date ____
4. ☐ Examiner's Comment Regarding Requirement for Deposit of Biological Material
5. ☐ Notice of Informal Patent Application (PTO-152)
6. ☐ Interview Summary (PTO-413), Paper No./Mail Date ____
7. ☒ Examiner's Amendment/Comment
8. ☒ Examiner's Statement of Reasons for Allowance
9. ☒ Other See Continuation Sheet.

EXAMINER'S AMENDMENT

1. An examiner's amendment to the record appears below. Should the changes and/or additions be unacceptable to applicant, an amendment may be filed as provided by 37 CFR 1.312. To ensure consideration of such an amendment, it MUST be submitted no later than the payment of the issue fee.

Authorization for this examiner's amendment was given in a telephone interview with Ms. Helena C. Rychlicki on November 28, 2005.

The application has been amended as follows:

Abstract

Please replace the abstract with the attached page.

In the specification:

Please replace pages 2-5 and 11 with the attached pages.

In the claims:

Claim 15, line 1, please delete "claim1" and insert thereof --claim 1--.

Claim 17, line 2, please delete "or phenyl" and insert thereof --, phenyl or--.

Reasons for allowance

2. The following is an examiner's statement of reasons for allowance:

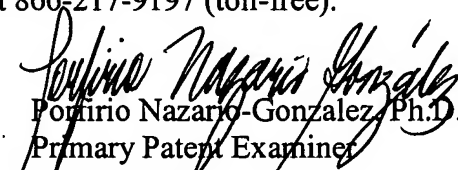
The instant claims are novel and unobvious over the prior art of record. The 2-step process for making a rac-diorganosilylbis(2-methylbenzo[e]indenylzirconium compound of the formula I in claim 1 is novel and unobvious over the prior art. The formation of an ansa-zircocene bisphenoxide complex of the formula IV, as an intermediate, in the formation of the metallocene of the formula I is not taught or disclose by the prior art of record.

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Any comments considered necessary by applicant must be submitted no later than the payment of the issue fee and, to avoid processing delays, should preferably accompany the issue fee. Such submissions should be clearly labeled "Comments on Statement of Reasons for Allowance."

Priority

3. Receipt is acknowledged of papers submitted under 35 U.S.C. 119(a)-(d), which papers have been placed of record in the file.
4. Any inquiry concerning this communication or earlier communications from the examiner should be directed to Porfirio Nazario-Gonzalez whose telephone number is 571-272-0641. The examiner can normally be reached on Mon.-Fri. (9:30 AM - 6:00 PM).
5. If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Johann R. Richter can be reached on 571-272-0646. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.
6. Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).


Porfirio Nazario-Gonzalez, Ph.D.
Primary Patent Examiner
Art Unit 1621

PNG

November 28, 2005

Continuation of Attachment(s) 9. Other: Replacement pages 2-5 and 11 and Abstract.

mixture of the ansa-metallocene compounds has to be followed by either a complicated separation of diastereomers or destruction of the meso form, which again approximately halves the yield. The total yield of pure rac-ansa-metallocene is therefore generally not more than 15-20%.

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A further disadvantage is the efficiency of the synthetic route. As described above, the ansa-metallocene compound has to be separated off from the alkali metal halides or alkaline earth metal halides formed as coproducts, and in some cases this proves to be difficult because of the low solubility of the ansa-metallocene compound, in particular in toluene, since the alkali metal
10 halides or alkaline earth metal halides are also virtually insoluble in organic solvents. This separation step therefore requires large amounts of solvent, which in turn has an adverse effect on the productivity and effectiveness of the synthetic route.

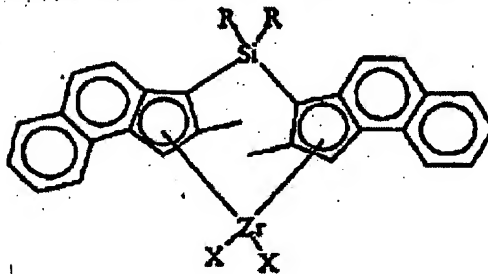
It is an object of the present invention to find a process for the selective preparation of racemic
15 metallocene complexes which are virtually free of the meso isomer.

We have found that this object is achieved by the process claimed in the independent process claim. Preferred embodiments of the present invention are obtained by combining the features of
20 the main claim with the features of the dependent, subordinate claims.

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The present invention provides a specific process for the diastereoselective synthesis of rac-diorganosilylbis(2-methylbenzo[e]indenyl)zirconium compounds of the formula I,

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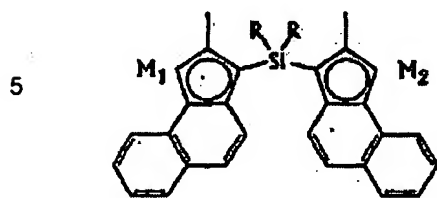


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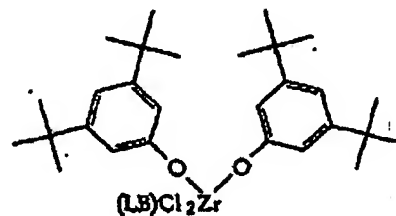
(I)

which comprises the following steps:

a) reaction of a compound of the formula II with a zirconium bisphenoxide complex of the formula III to form the ansa-zirconocene bisphenoxide complex of the formula IV,



(II)

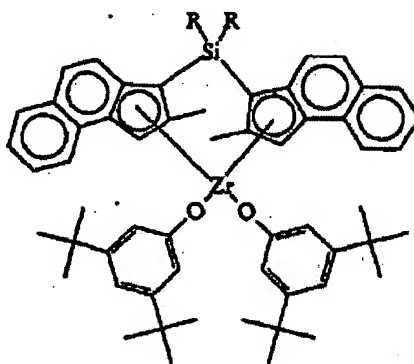


(III)

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(IV)

25 b) replacement of the phenoxide groups of IV by X using suitable replacement reagents to give the compound of the formula I;

where

the substituents X can be identical or different and are each F, Cl, Br, I, or linear, cyclic or branched C₁₋₁₀-alkyl; and

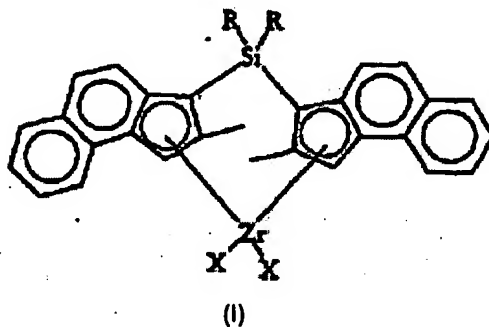
30 the substituents R can be identical or different and are each linear, cyclic or branched C₁₋₁₀-alkyl or C₈₋₁₀-aryl; and

LB is a suitable Lewis base, and

M₁ and M₂ are monovalent positive alkali metal ions or M₁ and M₂ together represent a divalent positive alkaline earth metal ion.

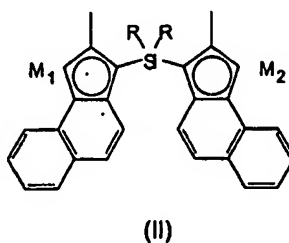
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A particularly preferred embodiment of the process of the present invention for the diastereoselective synthesis of rac-diorganosilylbis(2-methylbenzo[e]indenyl)zirconium compounds of the formula I,



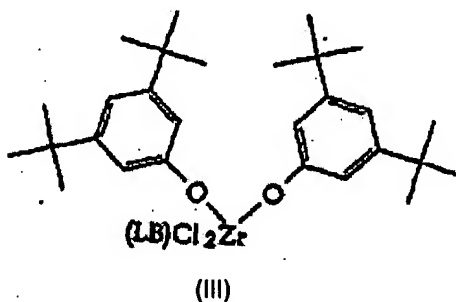
comprises the following steps:

- a) deprotonation of 2-methylbenzo[e]indene by means of a suitable deprotonating agent;
- b) reaction of the deprotonated 2-methylbenzo[e]indene with a diorganosilyl compound R_2SiY_2 , where the substituents R can be identical or different and are each linear, cyclic or branched C_{1-10} -alkyl or C_{6-10} -aryl and the leaving groups Y can be identical or different and are each F, Cl, Br or I, and subsequent repeat deprotonation by means of a suitable deprotonating agent, giving a compound of the formula II:

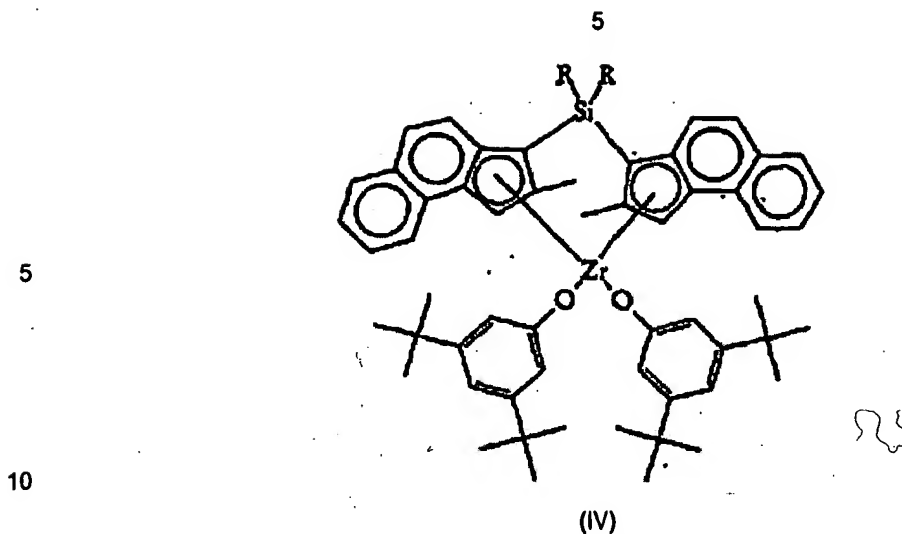


where M_1 and M_2 are monovalent positive alkali metal ions or M_1 and M_2 together represent a divalent positive alkaline earth metal ion;

- c) reaction of the compound of the formula II with a zirconium bisphenoxide complex of the formula III:



- where LB is a suitable Lewis base, to give a compound of the formula IV:



d) reaction of the compound of the formula IV with suitable replacement reagents so as to replace the phenoxide groups of IV by X to give the compound of the formula I, where the substituents X can be identical or different and are each F, Cl, Br, I or linear, cyclic or branched C₁₋₁₀-alkyl.

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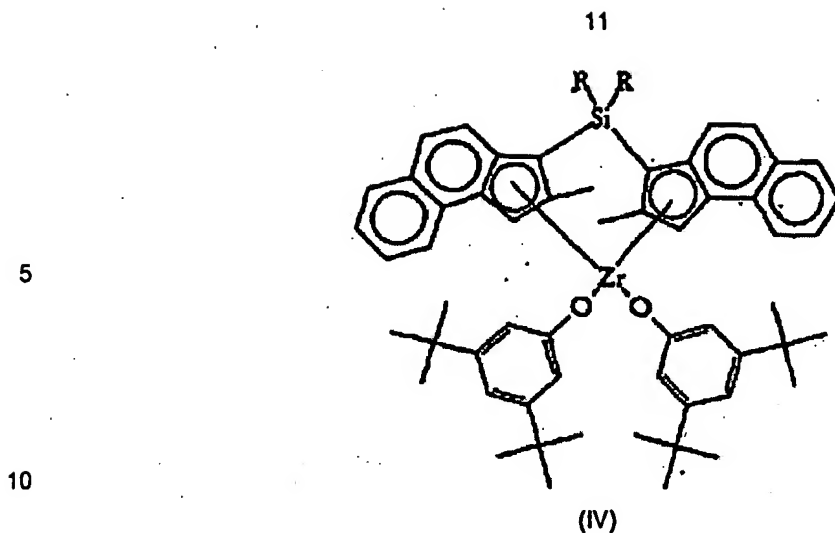
The process of the present invention is particularly preferably carried out with the intermediate IV being converted in the same reaction vessel in which it has been formed into the complex I by replacement of the phenoxide groups.

20 Furthermore, preference is given, according to the present invention, to the substituents R being selected from among methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl and phenyl and combinations thereof. The substituents X are preferably selected from among F, Cl, Br, I, methyl, ethyl, n-propyl, isopropyl, n-butyl and isobutyl, more preferably Cl and/or methyl. Preference is also given to M₁ and M₂ being selected from among lithium, sodium, potassium, rubidium or cesium ions or together representing magnesium. Particular preference is given to R being methyl or ethyl, X being Cl and LB being THF or DME, and M₁ and M₂ each being Li. The Lewis base LB used is preferably tetrahydrofuran (THF), dimethoxyethane (DME) or tetramethylethanediamine (TMEDA).

30 In the process of the present invention, a Lewis base, preferably THF or DME, may, if appropriate, be added once again in the replacement of the phenoxide groups of the complex IV.

The terms "meso form", "racemate" and thus also "diastereomers" and "enantiomers" are known in the context of metallocene complexes and are defined, for example, in Reingold et al., Organometallics 11 (1992), pages 1869 – 1876. For the purposes of the present invention, the term "virtually meso-free" or "racemoselective" means that more than 80%, preferably at least 90%, of a compound are present in the form of the racemate, particularly preferably at least 95%.

40 We have surprisingly found, according to the present invention, that diorganosilylbis(2-methylbenzo[e]indenyl)zirconocene compounds I can be obtained racemoselectively in a simple



where the substituents R can be identical or different and are each linear, cyclic or branched C₁₋₁₀-alkyl or C₆₋₁₀-aryl and are preferably selected from among methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl and phenyl and combinations thereof.

The racemic complexes I obtained according to the present invention, like those of the formula IV, can be used as catalysts or in catalyst systems for the polymerization and copolymerization of olefinically unsaturated compounds such as ethylene, propylene, 1-butene, 1-hexene, 1-octene, styrene. They can be used particularly advantageously in the stereoselective polymerization of prochiral, olefinically unsaturated compounds such as propylene and styrene. Suitable catalysts or catalyst systems in which the racemic metallocene complexes according to the present invention can function as "metallocene component" are usually obtained by means of compounds which form metallocenium ions, as described, for example, in EP-A-0 700 935, page 7, line 34, to page 8, line 21, and the formulae (IV) and (V). Further compounds capable of forming metallocenium ions are aluminoxanes (RAIO)_n such as methylaluminoxane, and also boron activators.

The racemic metallocene complexes of the formulae I and IV according to the present invention can also be used as reagents or as catalysts or in catalyst systems in stereoselective, in particular organic, synthesis. Examples which may be mentioned are stereoselective reductions or stereoselective alkylations of C=C double bonds or C=O, C=N double bonds.

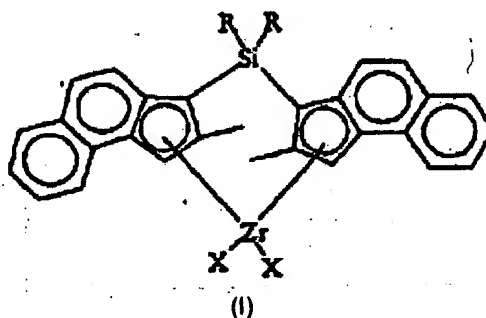
In the process of the present invention, the resulting complexes I and IV are obtained in a yield of about 30-80% of rac based on indene compound used.

A further significant advantage is that the process of the present invention can be carried out racemoselectively in a single-vessel process. For the present purposes, a single-vessel process is one in which no intermediates are isolated after the individual process steps. The further reaction can be carried out directly using the reaction product mixtures from the preceding step.

Abstract

The present invention relates to a specific process for the diastereoselective synthesis of rac-
5 diorganosilylbis(2-methylbenzo[e]indenyl)zirconium compounds of the formula I,

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15 by reacting the silyl-bridged bisindenyl ligand with a dihalozirconium bis(3,5-di-tert-butylphenoxide)-base adduct to form the diorganosilylbis(2-methylbenzo[e]indenyl)zirconium bis(3,5-di-tert-butylphenoxide) and subsequently replacing the phenoxide groups by X using
suitable replacement reagents to give the compound of the formula I; where the substituents X
20 can be identical or different and are each F, Cl, Br, I or linear, cyclic or branched C₁₋₁₀-alkyl; and
the substituents R can be identical or different and are each linear, cyclic or branched C₁₋₁₀-alkyl
or C₆₋₁₀-aryl; and also to the use of these compounds as catalysts.